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(75) Inventor/Applicant (for US only): BOSMAN, Joris [BE/BE]; Wezelsbaantje 29B, B-2230 Herselt (BE).			With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
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(54) Title: METHOD FOR THE PREPARATION OF ORGANIC CARBAMATES			
(57) Abstract			
Organic carbamates are prepared by the reaction of organic amines (preferably aromatic polyamines) with heteroatom-substituted alkyl carbonates. Said carbamates can be thermolysed into the corresponding isocyanates.			

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Method for the preparation of organic carbamates

The present invention relates to a method for the preparation of organic carbamates by reaction of amines with organic carbonates.

It is known to react amines with organic carbonates in order to obtain carbamates.

5 US-A 5.347.034 discloses a process for producing poly(O-alkylurethanes) of the diphenylmethane series by reacting the corresponding amines with dialkyl carbonates in the presence of a catalyst, such that the formed poly(O-alkylurethanes) crystallize out in a highly pure form upon cooling.

The production of the O-ethylcarbamate of TDI is described in EP-A 520.273.

10 EP-A 391.473 describes a process for producing carbamates using reduced amounts of catalyst by first reacting an amine with a (cyclo)alkyl carbonate in the presence of a carbamation catalyst to produce a mixture of a carbamate and an urea, further reacting the urea with carbonate to produce the corresponding carbamate, and finally recovering the carbamate from the reaction mixture.

15 In DE-A 3.202.690 a method for preparing aromatic urethanes is described by reacting aromatic amines and alkylcarbonates in the presence of an alcoholate of an alkali metal or an alkaline earth metal.

US-A 4.268.684 discloses a method for the preparation of carbamates by reacting an organic carbonate with an aromatic amine in the presence of certain zinc, tin or cobalt 20 salts which are only active at temperatures of at least 200° C whereas in US-A 4.268.683 zinc or tin salts are used which are soluble in the reaction mixture at the reaction conditions.

EP-A 48.371 describes the preparation of N,O-disubstituted urethanes by reacting primary amines with dialkylcarbonates in the presence of neutral or basic inorganic or organic 25 lead, titanium zinc or zirconium compounds.

The preparation of aliphatic carbamates using a sodium methoxide catalyst is disclosed in e.g. US-A 5.138.015 and US-A 5.315.034.

EP-A 752.414 concerns a process for the preparation of aromatic urethanes in the presence of a zinc and/or copper carbonate hydroxide catalyst.

5 In US-A 4.550.188 carbamates are prepared by heating an organic carbonate and an aromatic amine in the presence of aluminum as catalyst and a promoter comprising a combination of iodine and a mercury salt.

The synthesis and thermolysis of aliphatic fluorinated carbamates is described in JP-A 57.197.645.

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It has now surprisingly been found that carbamates can advantageously be prepared by reacting specific organic carbonates with amines.

The invention thus concerns a method for the preparation of carbamates comprising reacting amines with heteroatom-substituted alkyl carbonates.

15 The method of the present invention allows for the production of carbamates under mild reaction conditions, i.e. relatively low temperatures and pressures.

Typical examples of suitable carbonates are bis(2-isopropoxyethyl) carbonate, bis(1,3-dimethoxy-2-propyl) carbonate, bis(1,1-dimethoxy-2-ethyl) carbonate, bis(2-methoxy-1-propyl) carbonate, bis(2-methoxy-3-butyl) carbonate, bis(1-ethoxycyclopropyl) carbonate, bis(N,N-dimethylaminoethyl) carbonate, bis(2,2,2-trifluoroethyl) carbonate, bis(2,2,2-trichloroethyl) carbonate, bis(1,1,1,3,3-hexafluoroisopropyl) carbonate, bis(nonafluorotert.butyl) carbonate, bis(fluorophenyl) carbonates, bis(chlorophenyl) carbonates and polysubstituted halogenated phenyl carbonates.

Fluorine-containing carbonates, such as bis(1,1,1,3,3-hexafluoroisopropyl) carbonate, bis(2,2,2-trifluoroethyl) carbonate or bis(nonafluorotert.butyl) carbonate, are preferred.

Amine compounds which can be used in the present method include aliphatic, cycloaliphatic or aromatic mono-, di- or polyamines.

Suitable amines according to the process of the invention include, for example, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, 5 hexylamine, cyclopropylamine, cyclobutylamine, cyclohexylamine, laurylamine, stearylamine, phenylamine, 4-chlorophenyl amine, 2-fluorophenyl amine, 3,4-dichlorophenylamine, aniline, benzylamine, toylamine, diisopropyl phenylamine, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 2,2'-diaminodiphenylmethane and higher homologs (polyaminopolypheylmethanes), 2,4-toluenediamine, 2,6-toluene 10 diamine, m-phenylenediamine, 1,4-butylenediamine, 1,6-hexylenediamine, 1,5-naphthylene diamine, 1,4-cyclohexylenediamine, isophoronediamine, 2,2,4-trimethylhexamethylenediamine and mixtures thereof.

Preferred are aromatic di- or polyamines like toluenediamines, diaminodiphenylmethanes or polyaminopolypheylmethanes or any mixtures thereof.

15 The polyamines and the organic carbonates may be reacted in stoichiometric quantities. The use of an excess of organic carbonates however is preferred.

The method of the present invention may be carried out in the presence of a catalyst. Preferred are heterogeneous metal based catalysts, such as organic metal salts on an inert carrier support or metal based catalysts which form a metal compound which is present as 20 a precipitate during or after completion of the reaction.

Organic or inorganic salts which may be used include, for example, acetates, chlorides, propionates, isopropanoates, butanoates, 2-ethylhexanoates, n-octoates, isononanoates, benzoates, chlorobenzoates, naphthenates, stearates, itaconates, pivalates, phenolates, acetylacetones, alkoxides, C<sub>16</sub>/C<sub>18</sub>-alkenylsuccinates (ASA), C<sub>12</sub>-alkenylsuccinates 25 (DSA) and the like.

Preferred are alkanoates having from 1 to 15 carbons atoms.

Suitable catalysts include, for example, zinc catalysts such as zinc chloride, zinc acetate, zinc propionate, zinc octoate, zinc benzoate, zinc p-chlorobenzoate, zinc naphthenate, zinc stearate, zinc itaconate, zinc pivalate, zinc phenolate, zinc acetylacetone, zinc methoxide, lead catalysts like lead acetate and lead octoate, and tin catalysts like stannous 5 chloride, stannous octoate, and mixtures thereof.

Preferably, the metal in the catalyst is selected from the group consisting of Ti, Zr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Pb, Bi and Cd.

The heterogeneous metal based catalyst on the carrier may be made by impregnating the catalyst with or precipitating it on the carrier.

10 Suitable inert carrier supports include, for example, alumina, silica,  $TiO_2$ , clays, zeolites, resins, graphite and carbon. A preferred carrier comprises  $TiO_2$ .

The catalyst is generally used in amounts between  $10^3$  and 20 mole% based on the amount of amines used.

15 It has however been found that in some cases the presence of a catalyst is not required.

The reaction conditions largely depend on the type of reactants used.

The method may be carried out at atmospheric or superatmospheric pressures.

The pressure is preferably not more than 20 bar.

20 The reaction time is dependent on the temperature and on the type and quantity of the carbamate compound, but will normally be between 0.5 and 6 hours. Reaction times of less than 4 hours are common, and reaction times of not more than 3 hours have been achieved without any problem.

Generally, the reaction temperature will be between 20 and 300°C. Preferably, the method 25 of the invention is carried out at temperatures between 50 and 200°C.

The presence of a solvent is not required, but it may be added without adversely affecting the reaction.

Any solvent or mixture of solvents which is inert to the reactants under the reaction conditions may be employed.

5 Suitable solvents which may be employed include, for example, aromatic hydrocarbons such as benzene, halogenated aromatic hydrocarbons such as monochlorobenzene, ortho-dichlorobenzene or 1-chloronaphthalene, alkylated aromatic hydrocarbons like toluene, xylene, ethylbenzene, cumene or tetrahydronaphthalene, other functionalised aromatic hydrocarbons such as anisol, diphenylether, ethoxybenzene, benzonitrile, 10 2-fluoroanisole, 2,3-dimethylanisole or trifluorotoluene, alkanes such as n-pentane, n-hexane, n-heptane or higher or branched alkanes, cyclic alkanes like cyclopentane, cyclohexane or derivatives thereof, halogenated alkanes like chloroform, dichloromethane, carbontetrachloride, and alkanes with other functional groups like diethylether, acetonitrile, dioxane or mixtures thereof, and the like. Inert aromatic solvents 15 are preferred.

The alcohol which is released by the reaction of the carbonate with the amine may also advantageously be used as the solvent.

The presence of a catalyst is preferred under some circumstances, but the method may also be carried out without any catalyst being present.

20 In a further aspect, the invention relates to the preparation of organic isocyanates by thermolysis of the organic carbamates thus prepared.

The thermolysis may be carried out solvent-free or in the presence of a solvent. If a solvent is present, it may be the same as that used for the production of the carbamates.

25 The thermolysis reaction conditions, such as temperature and pressure, will depend on the type of carbamate and on whether a solvent is present or not.

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In the solvent-free method the temperature will preferably be between the melting point of the starting carbamate and 350°C.

When a solvent is present, the preferred temperature is between 50 and 200°C, and more preferably between 120 and 190°C.

5 The thermolysis may be carried out at atmospheric pressure, preferably under nitrogen.

However, in the absence of a solvent, the reaction preferably takes place under reduced pressure. In such instance, the pressure is preferably reduced to between 10<sup>-4</sup> and 50 mbar.

Superatmospheric pressures may sometimes be required, depending on the type of solvents used.

10 The synthesis and optional thermolysis of the organic carbamates can be conducted in any apparatus which can be equipped, if required, with agitation means and heating and/or cooling means to keep the temperature within the desired range.

The method of the present invention may be conducted batchwise or as a semi-continuous or continuous process.

15 One type of continuous operation is in a fluidized bed reactor in which a catalyst is carried into the reactor as a slurry in one or more of the reactants. Still another way of operating continuously is in a moving bed reactor in which the catalyst bed and the reactants pass concurrently or countercurrently to each other. A preferred type of continuous operation however is in a fixed bed reactor in which the reactants are passed over the catalyst bed.

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During the thermolysis alcohols are formed as by-product. These can be removed from the reaction mixture either continuously during or after completion of the reaction by e.g. distillation.

The isocyanates and alcohols thus obtained are generally of high purity and no additional treatment is required to further purify said products. Only the solvent, if present, needs to be removed.

If a particularly high grade of purity is required, the reaction products formed may be subjected to known purification methods, such as filtration, extraction, recrystallisation or distillation.

The invention is illustrated, but not limited, by the following example.

Example

Into a suitable flask equipped with a condenser and a thermometer, 0.1 g of diaminodiphenylmethane are dissolved in 1 g of 1,1,1,3,3,3-hexafluoro isopropanol. When the amine is dissolved, 3.5 g of bis(1,1,1,3,3,3- hexafluoroisopropyl)carbonate is added. This mixture is heated to reflux temperature (76°C) and stirred for 3 hours at this temperature. To the carbamate formed in this way, 5 g of ortho-dichlorobenzene (ODCB) are added. The mixture is heated and addition of monochlorobenzene (MCB) is started. At a temperature of 96°C the excess of the carbonate is distilled. Once the carbonate is removed, the mixture is allowed to heat up to 155°C. The temperature is controlled at this 10 temperature by continuous addition of the MCB. After 1 hour at 155°C an isocyanate is obtained. Infra-red analysis of this sample proved the formation of an isocyanate. GPC confirmed the formation of diphenylmethane diisocyanate.

## Claims

1. Method for the preparation of organic carbamates comprising reacting organic amines with heteroatom-substituted alkyl carbonates.
- 5 2. Method according to claim 1 wherein the amine is selected from the group consisting of toluenediamines, diaminodiphenylmethanes or polyaminopolypyrenylmethanes or mixtures thereof.
- 10 3. Method according to any one of the preceding claims wherein the reaction is carried out at a temperature between 50 and 200°C.
4. Method according to any one of the preceding claims wherein the reaction is carried out at a pressure of not more than 20 bar.
- 15 5. Method according to any one of the preceding claims which is carried out in the presence of an inert aromatic solvent.
6. Method according to any one of the preceding claims which is carried out in the presence of a heterogeneous metal based catalyst.
- 20 7. Method according to claim 6 wherein the catalyst comprises a metal selected from the group consisting of Ti, Zr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Pb, Bi and Cd.
8. Method according to claim 6 or 7 wherein the catalyst is supported on an inert carrier support or forms a precipitate containing said metal.
- 25 9. Method according to any one of claims 6-8 wherein the catalyst comprises an alkanoate having from 1 to 15 carbons atoms.

10. Method according to claim 8 or 9 wherein the carrier support comprises a member selected from the group consisting of alumina, silica,  $TiO_2$ , clays, zeolites, resins, graphite and carbon.
- 5      11. Method for the preparation of organic isocyanates by thermally decomposing the organic carbamates prepared according to any one of the preceding claims.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01693

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C07C269/04 C07C263/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HEINER ECKERT ET AL.: "Triphosgene, a Crystalline Phosgene Substitute" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION., vol. 26, no. 9, 1987, pages 894-895, XP002083416 WEINHEIM DE * page 895, table, compounds 2d, 2e * the whole document ---	11
A	EP 0 048 371 A (BAYER) 31 March 1982 (1982-03-31) cited in the application page 3, line 10 - page 8, line 20; claims; example 9 ---	1
A	EP 0 048 371 A (BAYER) 31 March 1982 (1982-03-31) cited in the application page 3, line 10 - page 8, line 20; claims; example 9 ---	1
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the International search report

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 520 273 A (BAYER) 30 December 1992 (1992-12-30) cited in the application the whole document -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr. Appl. No

PCT/EP 99/01693

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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				29-04-1982 25-03-1982 08-06-1982 01-05-1984 22-05-1982 26-01-1983
EP 520273	A	30-12-1992	DE CA JP	4121211 A 2072034 A 5201953 A
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